SUPPLEMENTARY MATERIAL

Reassessing spin-coupled (full generalized valence bond) descriptions of ozone using three-center bond indices

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S1. Additional results from various CASSCF and icMRCI calculations

Fig. S1. icMRCI LNOs and occupation numbers for ozone. Symmetry-related counterparts are identified in parentheses. These icMRCI calculations are based on a CASSCF(18,14) reference, as described in the paper.

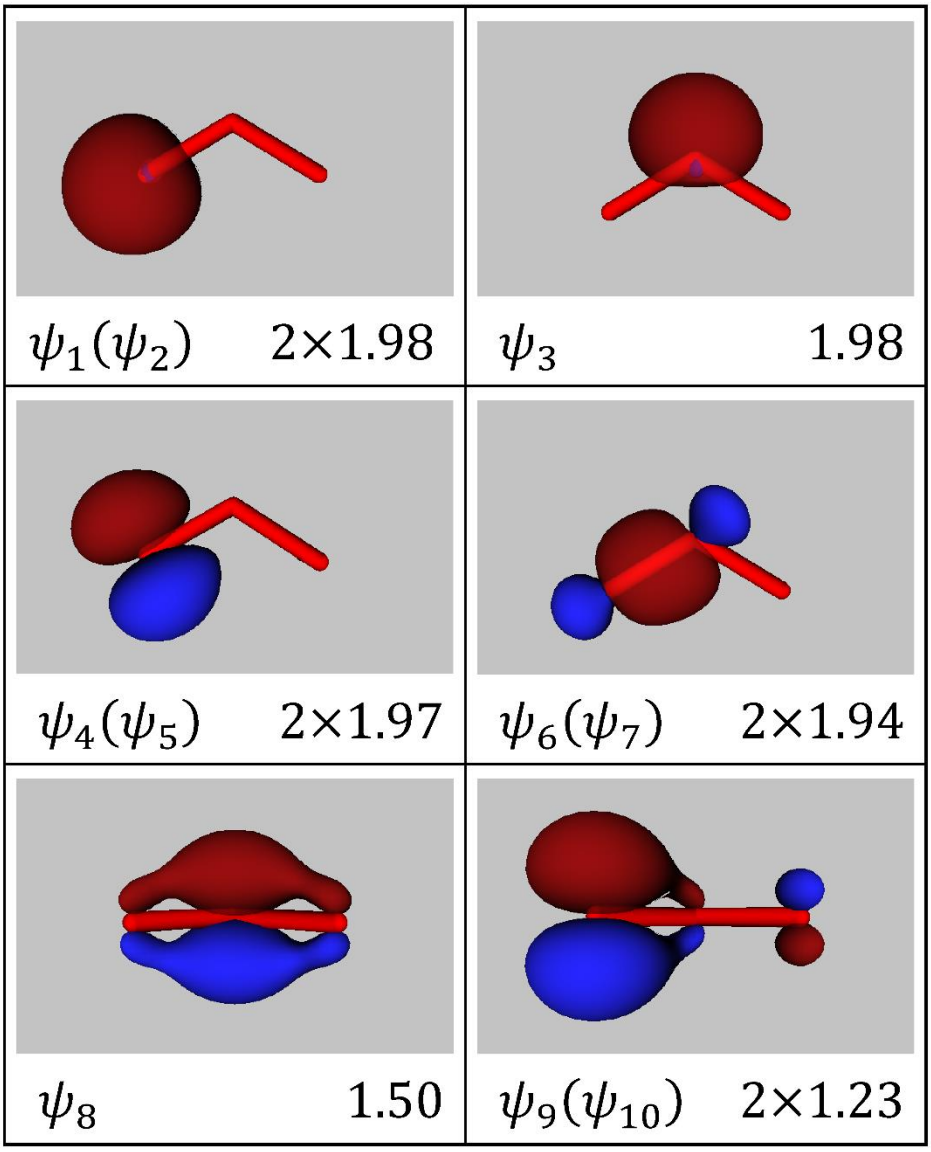


Table S1

Two- and three-center bond index values (*W* and *Y*), total energies (*E*) and dipole moments (μ) for various CASSCF and icMRCI wavefunctions that are described in the text. These icMRCI calculations are based on a CASSCF(18,12) reference.

Quantity	CASSCF(4,3)	CASSCF(18,12)	icMRCI
W_{12} σ-only		1.077	1.067
W_{12} π-only	0.382	0.433	0.422
W_{12}		1.510	1.489
W_{23} σ-only		0.145	0.146
W_{23} π-only	0.188	0.248	0.241
W_{23}		0.393	0.388
Y(O1,O2,O3) σ-only		−0.028	−0.027
Y(O1,O2,O3) π-only	−0.090	−0.154	−0.149
Y(O1,O2,O3)		−0.183	−0.175
E / hartree	−224.45379	−224.59583	−225.14213
μ / debye	0.227	0.556	0.537

S2. Additional results for combinations of $SC_x(10)$ components

Fig. S2. Active orbitals for the fully-optimized $SC_d(10)\oplus SC_I(10)$ combination: SC_d-like component, top two rows, and SC_I-like component, final two rows. Only the symmetry-unique orbitals have been shown in the case of SC_I.

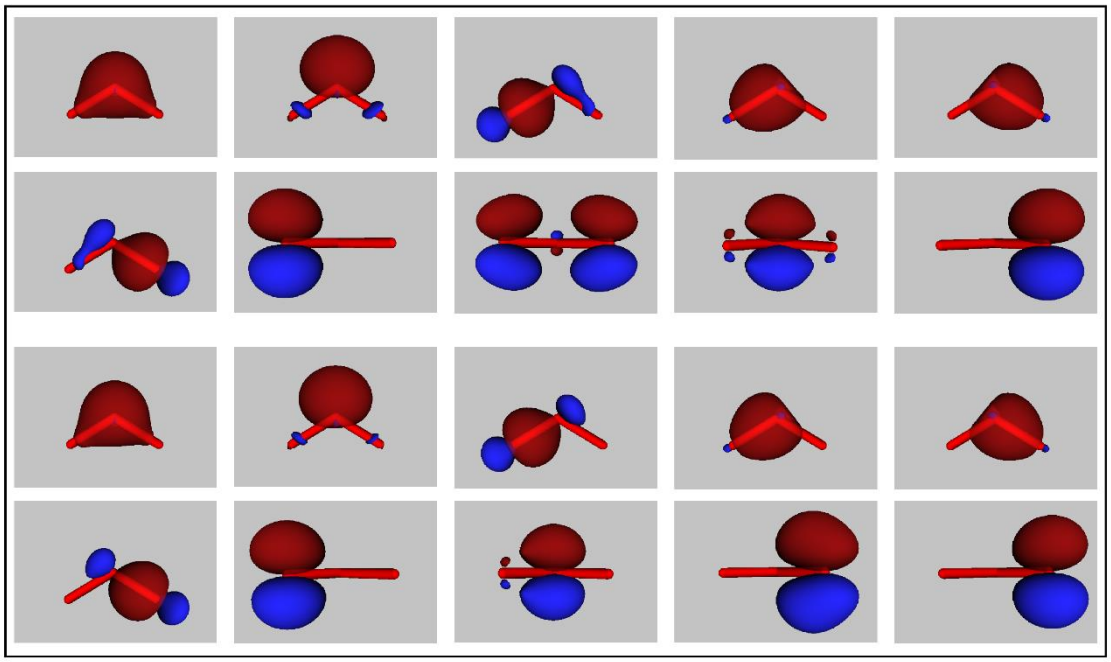
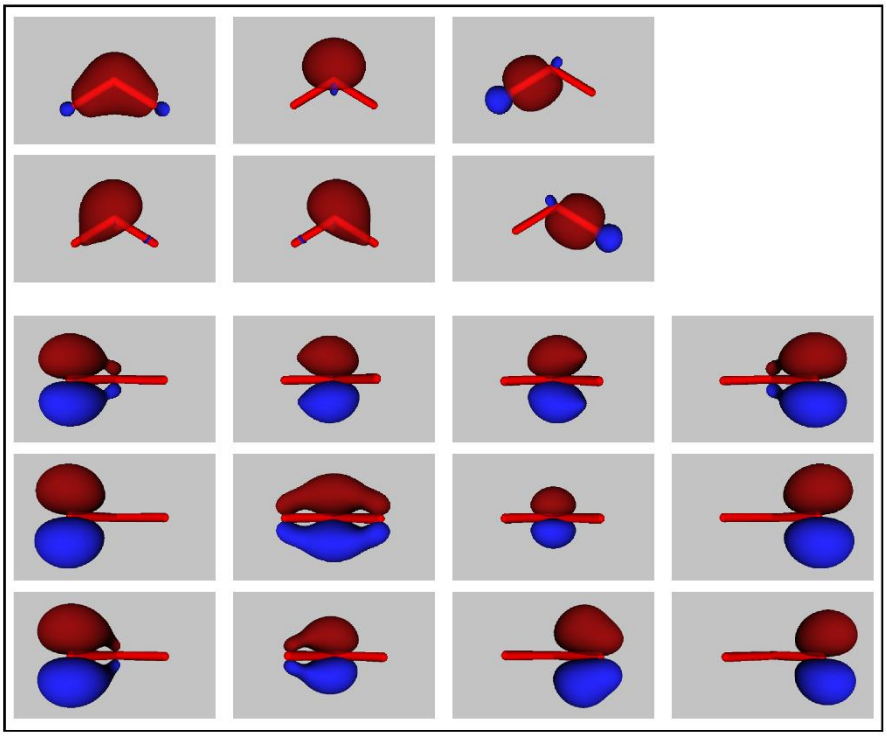


Fig. S3. Active orbitals for a fully-optimized $SC_c(10)\oplus SC_d(10)\oplus SC_I(10)$ construction: common set of active σ orbitals (top two rows) shown together with the π orbitals for the SC_c-like component (third row), for the SC_d-like component (fourth row) and for the SC_I-like component (final row). Only the symmetry-unique π orbitals have been shown in the case of SC_I.



S3. Values of *X*(O1,O2,O3)

Table S2

Values of *X*(O1,O2,O3):

(a) for various CASSCF and icMRCI wavefunctions that are described in the text (*cf*. the values of *Y*(O1,O2,O3) in Table 1). These icMRCI calculations are based on a CASSCF(18,14) reference.

Quantity	CAS(4,5)	CASSCF(18,14)	icMRCI
X(O1,O2,O3) σ-only		−0.030	−0.027
X(O1,O2,O3) π-only	−0.092	−0.146	−0.145
X(O1,O2,O3)		−0.176	−0.172

(b) for the various $SC_x(10)$ wavefunctions that are described in the text (*cf*. the values of *Y*(O1,O2,O3) in Table 2).

Quantity	$SC_c(10)$	$SC_d(10)$	$SC_I(10)$
X(O1,O2,O3) π-only	−0.097	−0.083	−0.149

(c) for various fixed-orbital combinations of $SC_x(10)$ configurations, as described in the text (*cf*. the values of *Y*(O1,O2,O3) in Table 3).

Quantity	$SC_c \oplus SC_d$	$SC_c \oplus SC_I$	$SC_d \oplus SC_I$	$SC_c \oplus SC_d \oplus SC_I$
X(O1,O2,O3) π-only	−0.096	−0.156	−0.150	−0.148

(d) for fully-optimized $SC_d \oplus SC_I$ and $SC_c \oplus SC_d \oplus SC_I$ combinations, with the latter based on a common set of active σ orbitals (*cf*. the values of *Y*(O1,O2,O3) in Table 4).

Quantity	$SC_d \oplus SC_I$	$SC_c \oplus SC_d \oplus SC_I$
X(O1,O2,O3) π-only	−0.117	−0.114

(e) for various CASSCF and icMRCI wavefunctions that are described in the text (*cf*. the values of *Y*(O1,O2,O3) in Table S1). These icMRCI calculations are based on a CASSCF(18,12) reference.

Quantity	CAS(4,3)	CASSCF(18,12)	icMRCI
X(O1,O2,O3) σ-only		−0.031	−0.027
X(O1,O2,O3) π-only	−0.083	−0.160	−0.152
X(O1,O2,O3)		−0.191	−0.179